SCIENCE AND TECHNOLOGY FOR ENERGY AND NATIONAL SECURITY

CRFNEWS

COMBUSTION RESEARCH FACILITY

May/June 2006 • VOL. 28, NO. 3

A detailed molecular-beam mass-spectrometric study and modeling of a low-pressure dimethyl ether flame

Dimethyl ether (DME) is considered to be a promising alternative to conventional liquid hydrocarbon fuels derived from petroleum. DME is easily manufactured from natural gas, and used as a replacement for, or as an additive to, conventional diesel fuel to obtain operational changes that result in significant reductions in both particulate and NO_x emissions. DME is also an ideal replacement for certain liquefied petroleum products used in stationary power generation, cooking, and residential heating in many places that currently are dependent on imported petroleum. To enhance the performance of DME in combustion applications, a more detailed knowledge of its combustion chemistry is required. To this end, a team of researchers set up an Advanced Light Source (ALS) low-pressure flame experiment to investigate DME's oxidation processes and compare this data to existing DME models.

Sandia researcher Nils Hansen, in cooperation with T.A. Cool of Cornell University, P.R. Westmoreland of University of Massachusetts, Amherst, and K. Kohse-Höinghaus,

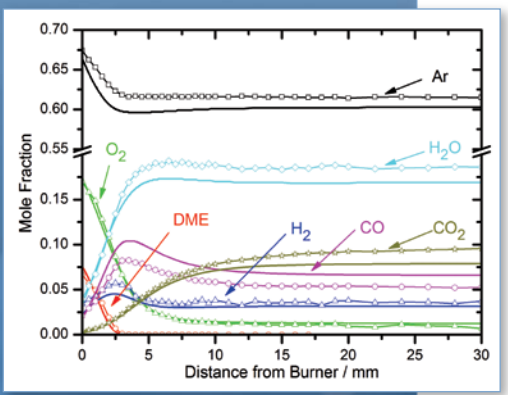

Figure 1. Mole fraction profiles for the major species DME, O_2, H_2, H_2O, CO, CO_2, and Ar.

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Sandia National Laboratories

An introduction to biodiesel

Recently, interest in biodiesel use in the U.S. has been growing due to: its potential to reduce dependence on imported petroleum, its potential to help mitigate possible negative impacts of global climate change by lowering net CO_2 emissions from the transportation sector (although there is some debate on this issue), and tax incentives and publicity that have resulted from the efforts of biodiesel advocates.

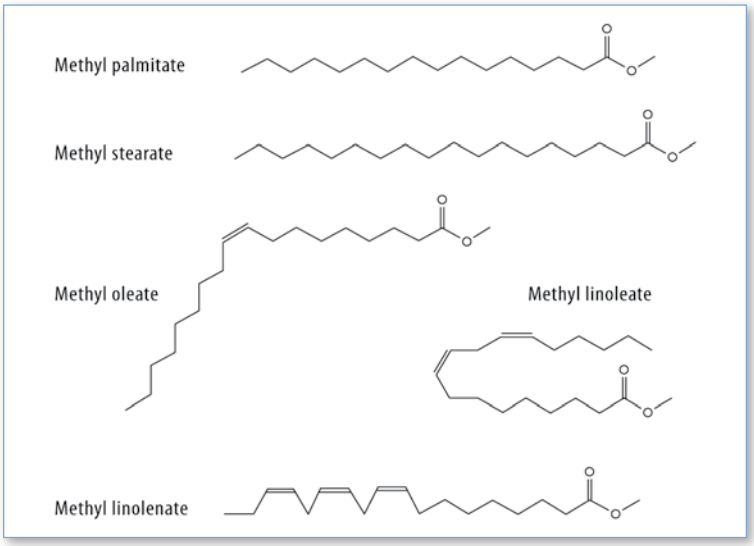

Figure 1. Molecular structures of the five methyl esters that typically comprise soy biodiesel.

Researchers at the CRF have been studying biodiesel for a number of years to better understand how and why biodiesel use could impact in-cylinder processes and as a result, the efficiency and emissions of advanced compression-ignition engines.

What is biodiesel?

Biodiesel is defined as "a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats". Biodiesel is typically created by reacting fatty acids with an alcohol in the presence of a catalyst to produce the desired mono-alkyl esters and glycerin. After reaction, the glycerin, catalyst, and any remaining alcohol or fatty acids are discarded from the mixture. The alcohol used in the reaction is typically methanol, although ethanol and higher alcohols also have been used. Most biodiesel currently produced in the U.S. is made from soybean oil, and soy biodiesel typically consists of the five methyl esters shown in Figure 1. While neat (i.e., 100%) biodiesel can be used, a blend of between 2 and 20% (by volume) biodiesel with diesel fuel is recommended to avoid engine-compatibility problems.

Biodiesel advantages and disadvantages

Biodiesel has a number of attractive attributes in addition to the aforementioned potential to reduce dependence on imported petroleum and to lower net greenhouse-gas emissions. Engine testing programs have shown that biodiesel fueling typically leads to lower emissions of particulate matter, unburned hydrocarbons, and carbon monoxide. Biodiesel typically has better lubricity and ignition quality relative to diesel fuel. Biodiesel is sulfur-free, so it won't poison catalytic aftertreatment systems. Furthermore, biodiesel is renewable.

Biodiesel is not a panacea, however. One notable disadvantage is that diesel-engine emissions of nitrogen oxides (NO_x) tend to increase by approximately 1% for every 10 vol% of biodiesel that is blended into diesel fuel. Biodiesel also can create problems in cold-weather conditions, because some of its constituent compounds can crystallize in the fuel. These crystals can plug fuel filters

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Biodiesel

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so that fuel cannot travel to the engine. In addition, biodiesel is often more susceptible to oxidative and biological instabilities than conventional diesel fuel, although these issues generally can be avoided by using the fuel promptly or by adding small amounts of stabilizer and biocide. Finally, impurities such as unreacted fatty acids or alcohol, as well as glycerin or catalyst left over from the production process, can cause accelerated wear or corrosion of engine components. Proper quality control is critical for avoiding unnecessary problems when biodiesel is introduced into widespread use.

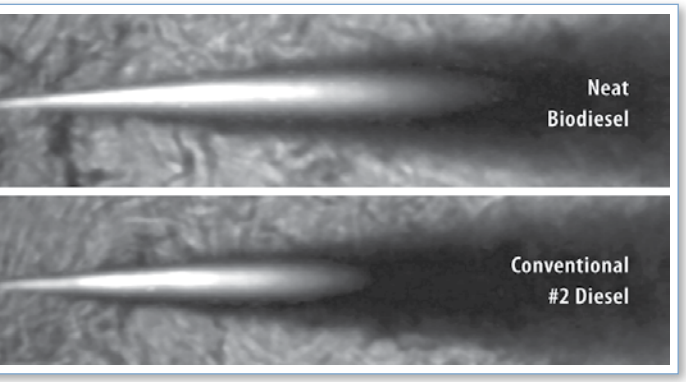


Figure 2. Superimposed images of Mie scattering from the fuel-jet core showing the liquid-penetration length and schlieren images showing the jet spreading angle. Image pairs are shown for neat biodiesel and conventional #2 diesel fuel. The liquid-penetration length is more than 30% longer for neat biodiesel than for #2 diesel fuel at this condition, which could lead to impingement of liquid fuel on in-cylinder surfaces. The ambient temperature and density at which the fuel is injected are 1000 K and 14.8 kg/m^3, respectively.

Past and current biodiesel research at the CRF

Early biodiesel research at the CRF showed that the elevated latent and specific heats of biodiesel compounds can lead to longer liquid penetration lengths within the combustion chamber than would be measured for diesel fuel injected into the same conditions; see Figure 2. This could cause impingement and adhesion of liquid fuel on in-cylinder surfaces, which could lead to increased fuel consumption and emissions, as well as oil degradation. A later study investigating molecular-structure effects on the soot-reduction characteristics of different oxygenated fuel compounds found that an ether structure was more effective than an ester structure (like that found in biodiesel) at attenuating in-cylinder soot concentrations in experiments. Subsequent reaction-path analysis provided an explanation by showing that more than 30% of the oxygen in the ester structure was unavailable for the prevention of soot-precursor formation.

Current biodiesel research in the CRF's Advanced Fuels Optical Engine Laboratory, led by principal investigator Chuck Mueller with co-investigators Ed Cheng (San Francisco State University) and Andre Boehman (Pennsylvania State University) investigates the underlying reasons behind observed increased NO_x emissions with biodiesel fueling. Hypotheses in the literature that explain the elevated biodiesel NO_x emissions include (1) an increased bulk modulus of biodiesel causing an advanced start of combustion, (2) a larger premixed-burn fraction, and (3) an increased stoichiometric adiabatic flame temperature. Recently, a study was conducted where a hydrocarbon (i.e., nonoxygenated) reference fuel was formulated to have the same ignition delay as neat biodiesel at a given operating condition. Figure 3 shows that even when the start of combustion and premixed-burn fraction were matched between the two fuels, NO_x emissions were still ~10% higher for the neat biodiesel fuel. Furthermore, computed stoichiometric adiabatic flame temperatures were identical for the reference fuel and a number of other oxygenated and nonoxygenated fuel components, including a biodiesel surrogate (methyl oleate). These results show that the three hypotheses above cannot fully explain the increased NO_x emissions with biodiesel fueling. Experiments to identify the primary source(s) of increased biodiesel NO_x emissions are currently underway, as are studies of low-temperature combustion strategies to control NO_x.

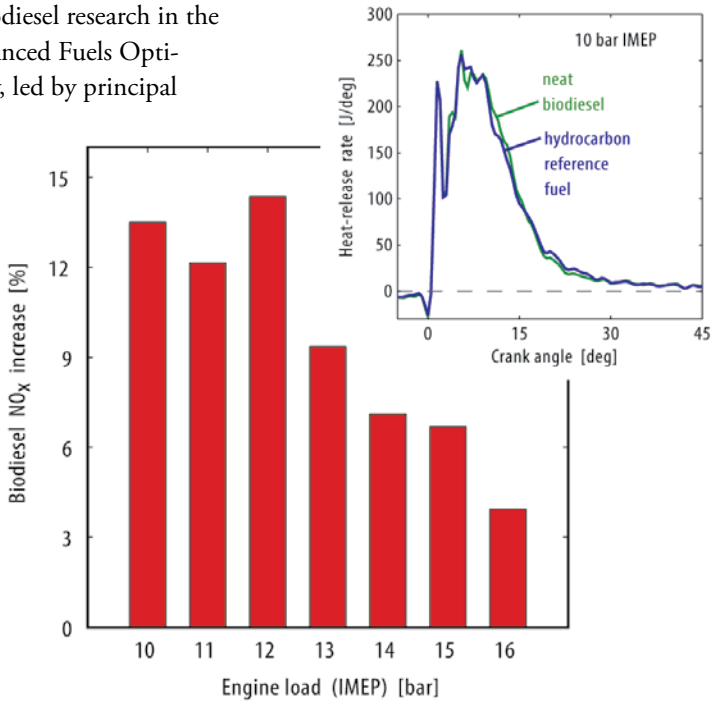
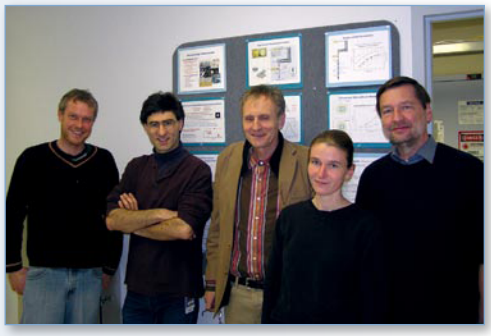


Figure 3. Measured NO_x emissions are ~10% higher on average when fueling with neat biodiesel relative to fueling with a hydrocarbon reference fuel, even when the start of combustion and premixed-burn fraction are matched between fuels (inset). The engine speed (800 rpm) and intake conditions also were the same for both fuels at each load point.

CRF researcher receives SAE award

Magnus Sjoberg, researcher in the CRF engine combustion group, received the Forest R. McFarland award from the Society of Automotive Engineers (SAE) at the SAE World Congress in Detroit. The award was given for his efforts and leadership as an organizer of technical sessions on HCCI combustion.



Berlin profs visit fiber laser lab

In January, Profs. Juergen Eichler and Ralph Hansen of the Berlin Technical University visited the fiber-laser laboratory in the CRF. Several students from the university have conducted their thesis research in the CRF. Georg Wien recently completed his studies and has accepted a job with a Finnish manufacturer of specialty optical fibers. Andrea Hansen is currently writing her thesis. From the left: Georg Wien (former student visitor), Dahv Kliner, Prof. Juergen Eichler, Andrea Hansen (current student visitor), and Prof. Ralph Hansen.

Sandia visitor program attracts local researcher

The CRF's visitor program, *http://www.ca.sandia.gov/crf/working/visitors/faq.php* attracts over 900 reseachers yearly from around the world. This particular visitor perched on the wall outside building 905 for two days in April, assessing the ground squirrel population. An experimentalist, she sampled a few. Sandia has its own wildlife site. *http://www.ca.sandia.gov/wildlife/*
Since 1994, more than seventy bird species, five species of amphibians and reptiles, and fifteen mammal species have been observed at Sandia California.

***Buteo jamaicensis* (Red -Tailed Hawk)**

CRF engine researchers receive SAE "best paper" award

Sandia researchers Paul Miles (left) and Lyle Pickett (right), as well as post-doctoral fellow Dae Choi (now at Hyundai Motors), and co-authors Sanghoon Kook and Choongsik Bae of Korea Advanced Institute of Science and Technology (KAIST) received the Society of Automotive Engineers (SAE) Horning Award for the best paper in 2005. The paper comprises research on advanced "clean diesel" combustion strategies conducted over the past two years at the CRF in collaboration with KAIST researchers. The Horning Award is the top international best paper award in the area of engine and fuels research and has been given annually by the SAE since 1939.

This is the sixth time Sandia's researchers have won this award since Sandia began engine research in the mid-1970s, more than any other company, institution, or university working in the engine/fuels research field during that time period.

A detailed molecular beam

(Continued from page 1)

Universität Bielefeld, Germany, measured species mole-fraction profiles in low-pressure premixed DME/O_2/Ar laminar flames using photoionization mass spectrometry with tunable synchrotron radiation and molecular-beam flame sampling. They then compared the results with flame model predictions based on a model developed by F. L. Dryer of Princeton University.

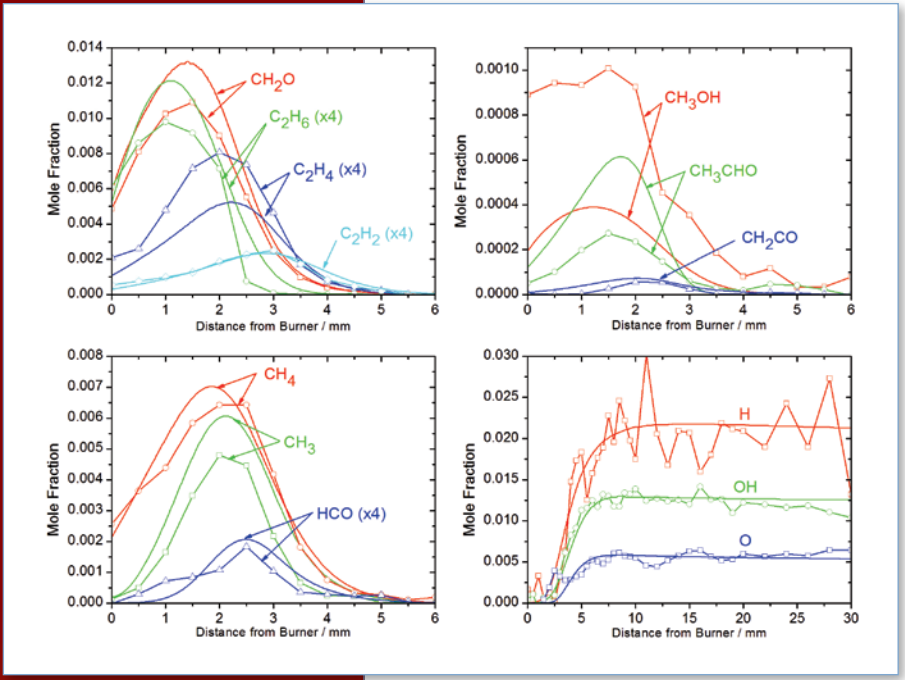


Figure 2. Mole fractions for intermediate and minor flame species.

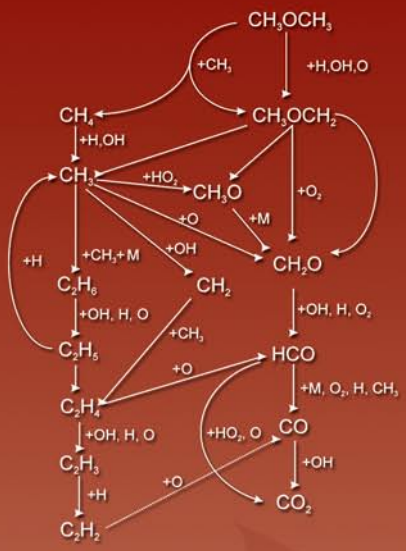


Figure 3. Simplified overview of important DME combustion processes. Species and dominant reaction paths are identified for dimethyl ether combustion.

How it works

The researchers used an instrument that consists of a low-pressure flame chamber, a differentially pumped molecular-beam flame-sampling system, and a linear time-of-flight mass spectrometer (TOFMS).

A premixed DME/oxygen/argon flame was stabilized at a pressure of 30 Torr on a flat-flame burner located inside a flame chamber. Flame gases were sampled along the flow axis with a quartz cone and collimated by a nickel skimmer to form a molecular beam at the entrance to the main test chamber. The burner could be moved towards or away from the fixed sampling cone to record mass spectra at any desired position from the burner face, through the luminous zone, and out into the burned gases. The molecular beam passes horizontally through the gap between the repeller and extraction plates of a conventional Wiley-McLaren linear TOFMS. The tunable, vacuum ultraviolet beam from the ALS intersects the molecular beam at the ionization source region between the repeller and extraction plates of the TOFMS. Tunable single-photon VUV ionization allows the unique identification of isomeric species by mass and ionization threshold. The Chemical Dynamics Beamline at the Lawrence Berkeley Laboratory ALS provides 8-17 eV photons with an energy resolution of 40 meV. Pulsed gating of the repeller plate voltage was used to propel ions up the flight tube to a multichannel plate detector. A multi-channel scaler records the TOFMS mass spectra.

Results

The mole fraction profiles for the major species DME; O_2, H_2, H_2O, CO, CO_2, and Ar shown in Figure 1 and are compared with flame model predictions. The major species mole fraction profiles determined experimentally were found to agree with the profiles predicted by kinetic modeling within the range of experimental uncertainties (±10-20%). No systematic differences were apparent.

The high-temperature DME reaction mechanism consists of 263 reversible elementary reactions and 46 species. This revised DME model is used to compare predictions against the new experimental data. The mechanism, thermochemistry, and transport parameters are available on the web (http://www.princeton.edu/~combust/).

Absolute mole fractions for the stable intermediates and the radicals HCO and CH_3 are compared with model predictions in Figure 2. Intermediate species present at the highest concentrations (CH_2O, CH_4, $C2H_6$, C_2H_4, and C_2H_2) are satisfactorily predicted within experimental uncertainties, while minor species (like CH_3OH and CH_3CHO) exhibit much larger discrepancies. DME is mainly consumed through the H-atom abstraction reactions by H, OH, O, and CH_3. The resulting methoxymethyl radical (CH_3OCH_2) then decomposes to CH_3O and CH_2O or reacts with O_2, CH_2O, CH_3O, and HO_2. Methyl radicals are formed primarily by dissociation of CH_3OCH_2 with smaller amounts resulting from reactions shown in Figure 3. A complicated sequence of events ensues, in which methyl radicals are destroyed, methane is formed and eventually removed from the flame (Figure 3). Ethane is formed entirely from the recombination of methyl radicals, generating ethyl radicals through subsequent reaction of ethane with H, OH, and O, which then decompose to yield ethene. About 50% of the ethene formation comes from ethyl radical decomposition; the other major source being $CH_3 + CH_2 \rightarrow C_2H_4 + H$. Ethene is consumed by the reactions with H, O, and OH. Vinyl then produces acetylene by reacting with H atom or by decomposition. Formyl radical, HCO, is generated from formaldehyde reactions with H, OH, and O_2. HCO then further reacts to yield CO, and finally, carbon dioxide is mainly produced by the key reaction $CO + OH \rightarrow CO_2 + H$. It can also be directly formed from HCO reacting with HO_2 or O.

DME combustion has many similarities to the combustion chemistry of the alkanes. Like propane, DME is a saturated molecule, which is only destroyed by H-abstraction, and the CH_3OCH_2 produced is mainly destroyed by beta-scission. Methyl and formaldehyde chemistry are identical for DME and propane. An important contrast is that beta-scission of CH_3OCH_2 predominantly breaks the fuel into smaller fragments, while isopropyl and n-propyl can easily go to propene.

The researchers also detected ethyl methyl ether ($C_2H_5OCH_3$), a feature that does not appear in any of the preexisting models for combustion processes of oxygenated hydrocarbon fuels.

Conclusion

The present results extend previous measurements of the composition of premixed DME/O2/Ar flames to include a dozen additional species, which include ethyl methyl ether, a molecule previously undetected in flame studies. The good agreement with model predictions lends support to both the experimental results and the existing DME flame model, which reveals reaction pathways quite analogous to alkane combustion. Now that the researchers have analyzed DME flames to an unprecedented level of detail, the next step is to compare this reference fuel with various DME/hydrocarbon fuels to investigate the effect of DME on the radical pool responsible for soot formation.

Bayesian inference with detailed physical models

The problem of inference is central to scientific advancement in a variety of fields. While progress in the detailed, first-principles modeling of physical systems has been considerable, it has also exposed a challenging and complementary task—inferring parameters, inputs, and even structural components of models from data. These quantities of interest are often separated from measurable data by complex physical processes (e.g., chemical reactions or scalar transport), and inference must therefore be indirect. In contrast to *forward* or predictive simulations, these problems of inference are known as *inverse problems*.

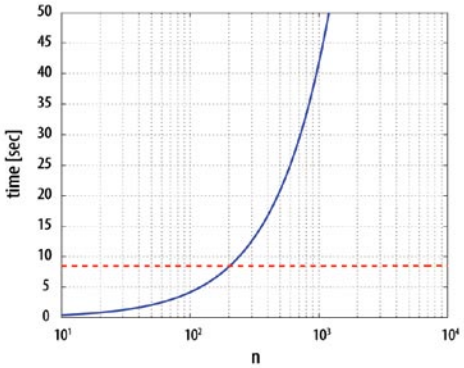


Figure 1. Computational time versus number of samples from the posterior distribution, for a simple source inversion problem. The solid line denotes direct sampling, while the dashed line reflects a polynomial chaos reformulation of the inverse problem. Typical applications will require 10^4–10^6 samples from the posterior.

Several factors render inverse problems difficult to solve. Real-world observations are often sparse and are inevitably affected by noise and measurement error. Inversion is typically ill-conditioned; that is, small errors in measurement can lead to enormous changes in the estimated model or model parameters. Additionally, multiple models may match a given set of data, or perhaps no feasible model may match the data.

Recent work by CRF researchers Youssef Marzouk and Habib Najm has focused on a probabilistic setting for inverse problems, and in particular, on Bayesian approaches. Bayesian statistics provide a rigorous foundation for inference from noisy data and stochastic forward models, a natural mechanism for incorporating prior information or constraints, and a quantitative assessment of uncertainty in the inferred results. Indeed, the output of Bayesian inference is not a single value for the model parameters, but rather a probability distribution that summarizes all available information about the parameters. From this posterior distribution, one may estimate means, modes, and higher-order moments; compute marginal distributions, or make additional predictions by averaging over the posterior. Probability in the Bayesian context reflects one's degree of belief in a proposition, and the posterior distribution is thus a complete description of uncertainty in the inverse solution, conditioned on the data. For instance, parameters that are known with great certainty will have very narrow posterior distributions, while parameters less constrained by the data may have broader posterior distributions. Other possibilities include multi-modal distributions, which reflect multiple distinct outcomes that are compatible with the data. (See Figure 2.)

Bayesian approaches to inverse problems have received much recent interest, with applications ranging from geophysics and climate modeling to heat transfer. The primary computational challenge in these areas is to extract information from the posterior density. Most estimates take the form of integrals over the posterior. In limited cases, these may be computed with asymptotic methods or with quadrature, but Markov chain Monte Carlo (MCMC) remains the most general and flexible technique for exploring complex and high-dimensional distributions. All of these methods, however, require an evaluation of the likelihood at many values of the model parameters. Evaluating the likelihood requires solving the forward problem. Detailed physical models (described by partial differential equations, for instance) can make each single evaluation computationally expensive. For MCMC simulations requiring 10^4–10^6 samples, the total cost of these forward evaluations quickly becomes prohibitive.

Marzouk and Najm have developed new theoretical and computational tools to address these challenges. Their approach, based on stochastic spectral methods for uncertainty propagation, reduces the cost of evaluating the posterior density by several orders of magnitude and thus enables Bayesian inference with complex and realistic physical models.

The efficient forward propagation of uncertainty—that is, from model parameters to model predictions—is a central challenge of uncertainty quantification (UQ). Strong parallels exist between stochastic UQ and Bayesian inversion. A simple approach to UQ is Monte Carlo simulation: sampling known distributions of the model parameters to obtain statistics or density estimates of the model predictions. Each sample requires a solution of the forward model, and with complex models, this sampling approach is computationally intensive. A useful alternative is to employ spectral representations of uncertain parameters and field quantities, specifically polynomial chaos (PC) expansions for random variables and processes. These representations lead to a reformulation of the governing equations of the forward model, but this reformulated system is solved only once.Depending on model nonlinearities and the necessary size of the PC basis, this computational effort may be orders of magnitude less costly than sampling.

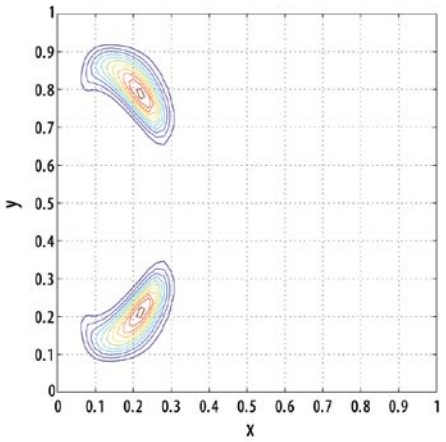


Figure 2. Features of a Bayesian solution with limited or degenerate data. What if sensors in the source inversion problem are distributed along a horizontal line? Then they cannot distinguish between a source above the line or below it. The posterior density, represented here by contours, is bimodal, reflecting two separate regions where the source may be located.

Recent work by Marzouk and Najm has formalized the connections between Bayesian

(Continued on page 6)

Bayesian inference (Continued from page 5)

estimation and the forward propagation of uncertainty. In particular, using PC to propagate a wide range of uncertainty—e.g., prior uncertainty—through the forward problem, and sampling the resulting spectral expansion, enables a substantially more efficient Bayesian solution of the inverse problem.

This process involves: (1) constructing PC expansions for each unknown parameter, according to probability distributions that include the support of the prior; (2) substituting these expansions into the governing equations and using Galerkin projection to obtain a coupled system of equations for the PC mode strengths; (3) solving this system (see Figure 3); and (4) forming an expression for the posterior density based on the resulting PC expansions of forward model predictions, then exploring this posterior density with an appropriate sampling strategy. In this scheme, sampling can have negligible cost; nearly all the computational time is spent solving the system in step 3.

This new approach has been demonstrated on inverse diffusion problems arising in contaminant source inversion. Source inversion is a problem with key homeland security and environmental applications. Given a sparse set of concentration measurements—from sensors scattered throughout a building or city, for instance—one would like to find the sources of a toxin or contaminant that has spread via time-dependent convection and/or diffusion. Specific parameters to infer include the number of sources, their strengths, and their locations. More generally, this corresponds to inferring a spatially distributed and time-dependent source field. In keeping

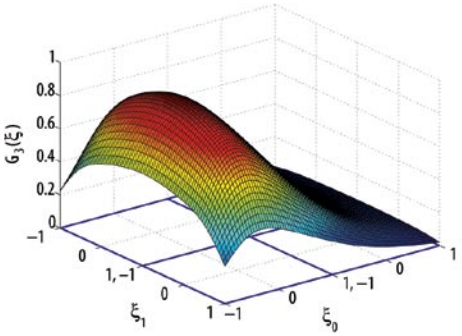


Figure 3. A single component of a stochastic forward solution with two unknown parameters, shown as a surface response on four quadrants of prior support.

with the Bayesian approach, one would like more than just a single "best" estimate of this source field; the method also characterizes the uncertainty surrounding this estimate.

In two-dimensional transient source inversion problems, the new stochastic spectral formulation reduces the cost of each posterior evaluation by nearly three orders of magnitude, so that sampling of the polynomial chaos-reformulated problem is very rapid. (See Figure 1.) Error in the posterior decreases rapidly with increasing order of the PC basis; convergence in entropic measures is exponentially fast. MCMC sampling of the posterior offers considerable freedom in choosing the PC basis and the initial transformation defining the stochastic forward problem, but a detailed exploration of posterior errors suggests guidelines for ensuring accuracy and computational efficiency.

Current work involves extending the Bayesian approach to more complex inverse problems. For instance, inverse problems with additional model uncertainties—uncertain parameters that may be marginalized in the posterior—are quite amenable to a Bayesian solution with polynomial chaos acceleration. Marzouk and Najm are also investigating issues of model reduction in high-dimensional inverse problems, e.g., inverse problems with spatially-extended input parameters, again using stochastic spectral approaches. Future work may apply Bayesian inversion to more fundamental studies of the mixing properties of turbulent flows, using stochastic models of scalar advection. And finally, these mathematical tools will be extended to structural inference—estimating model structures, such as kinetic network topologies, from data. These discrete model-building problems constitute a challenging and fertile ground for Bayesian inference.

CRF News is a bimonthly publication of the Combustion Research Facility, Sandia National Laboratories, Livermore, California, 94551-0969.
ISSN 1548-4300

Director ..... Terry Michalske
Editor ..... Wendy Wolfson
Graphic Artist ..... Daniel Strong
Photography ..... Daniel Strong/Various Photographers

Subscriptions are free. Subscriptions and address changes to Wendy Wolfson, wwolfs@sandia.gov

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